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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

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INTERNATIONAL APPLICATION NO.
PCT/GB99/01236INTERNATIONAL FILING DATE
22 April 1999PRIORITY DATE CLAIMED
22 April 1998

TITLE OF INVENTION

Adhesive and Encapsulating Material with Fluxing Properties

APPLICANT(S) FOR DO/EO/US

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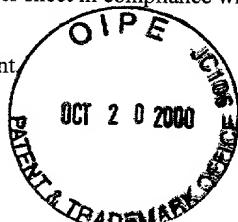
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

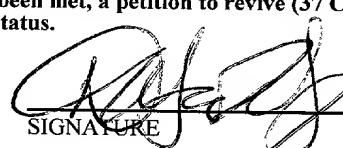
1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. A copy of the International Search Report (PCT/ISA/210).
8. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
9. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. A **FIRST** preliminary amendment.
16. A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. A substitute specification.
18. A change of power of attorney and/or address letter.
19. Certificate of Mailing by Express Mail
20. Other items or information:

A copy of the annexes to the International Preliminary Examination Report (pages 15-21 containing claims 1-42)



U.S. APPLICATION NO. (IF KNOWN) 09/673992	INTERNATIONAL APPLICATION NO. PCT/GB99/01236	ATTORNEY'S DOCKET NUMBER 1118-5 PCT/US		
21. The following fees are submitted:		CALCULATIONS PTO USE ONLY		
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00				
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$860.00		
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 \$0.00		
CLAIMS		NUMBER FILED	NUMBER EXTRA	RATE
Total claims	49	- 20 =	29	x \$18.00 \$522.00
Independent claims	2	- 3 =	0	x \$80.00 \$0.00
Multiple Dependent Claims (check if applicable).		<input checked="" type="checkbox"/>		\$270.00
TOTAL OF ABOVE CALCULATIONS =		\$1,652.00		
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).		<input type="checkbox"/>		\$0.00
SUBTOTAL =		\$1,652.00		
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 +		\$0.00
TOTAL NATIONAL FEE =		\$1,652.00		
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/>		\$0.00
TOTAL FEES ENCLOSED =		\$1,652.00		
		Amount to be: refunded		\$
		charged		\$
<input checked="" type="checkbox"/> A check in the amount of \$1,652.00 to cover the above fees is enclosed. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 08-2461 A duplicate copy of this sheet is enclosed.				
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.				
SEND ALL CORRESPONDENCE TO:				
Ronald J. Baron, Esq. Hoffmann & Baron, LLP 6900 Jericho Turnpike Syosset, New York 11791		 Daniel A. Scola, Jr. NAME _____ 29,855 REGISTRATION NUMBER _____ 20 October 2000 DATE _____		

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09/673992
526 Rec'd PCT/TTD 20 OCT 2000

ADHESIVE AND ENCAPSULATING MATERIAL WITH FLUXING
PROPERTIES AND USE THEREOF IN UNDERFILL TECHNOLOGY

5 This invention relates to electrical
interconnection methods in electronic circuitry and
more particularly to flip chip attachment and
encapsulation of both naked semi-conductors and chip
scale packages (CSPs). The technology is commonly
10 referred to as underfill technology.

As is noted in US-A-5 128 746, solder bump
interconnections when attaching chips to electronic
circuitry eliminate the expense, performance
limitations, low productivity and poor space
15 utilisation of wire bonding. As circuit density
increases occur, while circuit board and assembly sizes
continue to shrink, so-called flip-chip interconnection
using solder bumps has proved to be the most suitable
technique for satisfying such demands.

20 With the most common form of flip-chip
interconnection, solder bumps are placed on terminals
of the integrated circuit being produced while the
substrate for the integrated circuit is still in the
form of a small wafer or die. Commonly, the eutectic
25 Sn/Pb 60/40 or a high melting point alloy such as Sn/Pb
3/97, which is known to have been employed in the IBM
C4 process, is employed as solder material. The die or
wafer carrying the integrated circuit is to be joined
to a substrate and for this purpose the die or wafer
30 will be inverted (hence the term flip-chip). It is
current manufacturing practice to place a flux or
solder paste on the substrate. This material will
promote the adhesion of the die to the substrate during
reflow of the solder bump. During reflow, the assembly
35 produced is subjected to a temperature sufficient to
melt or collapse (C4 process) the solder bump and form

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the required interconnections. The flux residue must then be removed to prevent corrosion occurring to the die and, importantly, to allow free ingress of a subsequent underfill resin which is to encapsulate the various semi-conductors of the electronic circuitry produced.

For this latter purpose, an underfill encapsulant resin is applied around and under the die following reflow and flux removal. The very small gap between the die and substrate must be completely filled in order to provide environmental protection for the device. The filling of this gap is dependent on capillary action of the encapsulant material between the integrated circuit and substrate. The filling of the gap has proved to be a procedure which is very time consuming, expensive and difficult to achieve in the desired quality and is generally an unreliable procedure, particularly when a relatively large die is used. Moreover, the low viscosity of encapsulant material needed to ensure capillary action runs counter to the need to control thermal expansion and thermal conductivity by filling the encapsulation resin with ceramic powder which generally increases the viscosity of the resin. A solution to this problem has been to heat the substrate/component assembly to reduce initially the viscosity of the underfilling encapsulant resin. Temperatures must be precisely controlled and the process is difficult to control since the elevated temperature triggers the curing mechanism thus raising viscosity prematurely. For these various reasons, the underfilling process currently employed has low productivity and high space/equipment needs.

In the aforementioned US-A-5 128 746, it is proposed to add a fluxing agent to a cross-linking agent - containing encapsulant resin, the encapsulant resin being dispensed onto the substrate before the

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integrated circuit-carrying chip is placed in the encapsulant resin for reflow. US-A-5 128 746 discloses the use of certain strong organic dicarboxylic acids as examples of commercially available fluxing agents. A fluxing encapsulant resin of such type has three very serious drawbacks which compromise the integrity of the interconnection. Free acid remains in the encapsulant after reflow and can and will attack and corrode metal present, especially on the die or wafer. This problem is exacerbated by the decreased environmental resistance of such adhesive composition due to the presence of unreacted resin. As the adhesive composition has relatively low resistance to humidity and moisture, the corrosion problem is thus intensified. Moreover, the addition of acids of the stated type to epoxy resin adhesives compromises the stability of the adhesive, greatly reducing pot life and making cure characteristics variable. This will have a major effect on reliability and process control.

Finally, it is known that salts formed during fluxing of materials by reaction between metal oxides and fluxing agent and containing various metals including tin and lead can have a catalytic action on polymer materials thus causing a premature cure of the polymer prior to reflow of the solder.

It is an object of this invention to provide for the use of a thoroughly curable adhesive which does not suffer the problem of unreacted acid remaining in the encapsulant after reflow or the problem of pre-cure of the polymer due to salts formed during fluxing.

In one aspect, this invention provides a thermally curable adhesive composition which comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent; and

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5 (b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

10 which composition is thermally curable when heated to temperature range extending from the liquidus temperature of the alloy Sn/Pb 60/40 up to the liquidus 15 temperature of the alloy Sn/Pb 3/97 and in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures in the range of from 20-25°C.

15 According to a second aspect of the present invention there is provided a method of producing an electronic device which comprises opposing an electrical component having a surface carrying a plurality of electrical terminations, each termination including a solder bump, and a component-carrying 20 substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive 25 composition being applied to said surface of the electrical component and/or to the substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in 30 thermoset polymer produced in situ from monomer or polymer in the adhesive composition, in which method (1) the thermally curable adhesive composition comprises:

35 (a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to

the action of a chemical crosslinking agent; and
(b) a chemical crosslinking agent for said
polymer, the crosslinking agent having fluxing
properties and exhibiting no reactivity, or
exhibiting very restricted reactivity with the
polymer without the action of a catalyst and/or
heat; and

5 which composition is thermally curable when the
material of the solder bump is molten and in the
presence of a catalyst for the crosslinking of the
polymer with the crosslinking agent and is storage and
reaction stable in the absence of such catalyst and at
temperatures in the range of 20-25°C and (2) catalysis
10 of crosslinking of the thermally curable adhesive is
achieved by metal oxide removed from metal surfaces by
the fluxing composition and/or salts formed by reaction
15 between metal oxide and crosslinking agent.

20 This method uses novel adhesive compositions which
are preferably compositions of the first aspect of the
present invention.

25 A crosslinking agent to be employed in the
practice of the present invention will have fluxing
properties so as to enable it to remove oxides from the
material with which it is in contact, i.e. die and
substrate metallisation and, more particularly, solder
30 metal, thereby allowing solder joint formation. The
crosslinking agent, when present in sufficient amount,
is to be capable of complete reaction with
thermosetting polymer to neutralise, i.e. react with
35 all reaction sites of the polymer. The design of the
adhesive is preferably intended to ensure absence of
residual cross-linking agent therein and hence
equimolar quantities of polymer and crosslinking agent
are generally used. However, excess cross-linking
agent is not a problem in the practice of this
invention. Although it has the potential to corrode

metal surfaces which are normally accessible via pinholes which are present unavoidably in resin, now any excess cross-linking agent remains trapped in the polymer matrix together with catalyst so that corrosion of metal is not a problem. The composition itself is storage and reaction stable until heated to a temperature at which the latent reaction catalyst effectively causes the crosslinking agent to cure the thermosetting polymer and at which temperature the crosslinking agent will have melted and dissolved in the polymer or monomer.

Thus, the present invention provides for the use of chip underfill and encapsulation adhesive compositions having fluxing properties which enable one to achieve overall a rugged structure with protection of integrated circuits which have been previously solder bumped and then flip chip connected to a substrate with a metallisation pattern. During reflow, the fluxing achieved with the crosslinking agent allows metallic interconnection to be achieved between solder bump and metallisation pads on the substrate. The adhesive composition then reacts and cures to provide a fully adhered encapsulate underfill that is non-corrosive and environmentally resistant. The adhesive compositions themselves are stable and provide a long storage life at ambient temperatures, that is 20-25°C, while maintaining predictable processing characteristics. The adhesive compositions lack the substantial debilitating defects in the hitherto known compositions by providing a means for predepositing the underfill and eliminating separate fluxing and cleaning. The adhesive composition may be modified to optimise CTE, glass transition temperature (Tg), elasticity modulus and thermal conductivity without detriment to the aforementioned benefits or detriment to the required rheological properties which allow for

ease of deposition, for example by syringe dispensing. In addition, curing is achieved readily during any suitable thermal treatment, for example during reflow soldering. The underfill may only be partially cured after one or several solder reflow cycles, thus enabling ease of reworking of the device. Full cure is then achieved in a separate post-cure heat application. Alternatively, full cure may be obtained from one or two reflow cycles if reworkability is not required.

Insofar as the solder is concerned, this may consist of one or more metals which provide a suitable low melting point material. The metals employed are typically selected from tin, lead, bismuth, cadmium, zinc, gallium, indium, tellurium, mercury, thallium, antimony and selenium. The preferred such metal is tin or a tin/lead alloy. Specific examples of solders which may be employed are the aforementioned eutectic Sn/Pb 60/40 and the high melting point Sn/Pb 3/97.

The thermosetting polymer or monomer utilised in the compositions employed in the method of this invention is an adhesive substance which is preferably liquid at ambient temperature. Thus one may utilise a reactive polyester or an epoxide monomer or polymer such as an epoxy Novolak or epoxide precursor thereof. A preferred epoxy resin is either a diglycidyl ether of bisphenol A or a diglycidyl ether of bisphenol F. In preferred practice, such an epoxy resin is a B-stage resin or a resin which may be "B-staged" after application, thereby making it possible for there to be a delay before bringing together the component and the substrate. Other preferred epoxy materials to use are substances from the Araldite series of Ciba-Geigy Resins, such as the trifunctional epoxide MY10510 and the difunctional cycloaliphatic epoxide ERL 4221 which may be used singly or in admixture. The Araldite MY10510 may be replaced by Aradite MY9512, a tetra-

functional epoxide-based resin. MY9512 may be used alone, too, as may the trifunctional epoxide-based resin MY10510. The composition of the invention may also contain a monomer precursor for a polymer, e.g. an epoxide compound when an epoxy resin is required.

5 Mixtures of such epoxy materials may also be used.

The crosslinking agent with fluxing properties is usually solid at ambient temperature, but, provided it meets the reactivity requirements set out above for crosslinking agents of adhesive composition to be used this invention, it can also be liquid at ambient temperatures. The crosslinking agent is preferably a di- or polycarboxyl compound which is unreactive at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperatures, and such cross linking agents are generally referred to hereafter as polyacids. The cross-linking agent is preferably solid for this reason. Such polyacids serve as a fluxing agent for the oxide material present on the solder, which metal oxide is a catalyst for reaction between an epoxy resin and the carboxyl groups of the polymer at elevated temperatures. Such polyacid may be in particular a carboxylated polymer, a multifunctional polyanhydride or a long chain (C_8 or greater, preferably C_{10} or greater) polycarboxylic acid, preferably dicarboxylic acid. These acidic reactive compounds having a functionality greater than 1 provide multiple reaction sites, with epoxy resin serving to create a macromolecule that provides adhesion. A particularly preferred example of a polymer containing two or more carboxyl groups which may be employed is a styrene-acrylic acid copolymer. A preferred dicarboxylic acid is dodecanedioic acid (DDDA).

30 35 The polyanhydrides which may be used as cross-linking agent with fluxing properties in the practice

of this invention and which are preferably solid include polyazelaic polyanhydride and polyadipic polyanhydride. These materials provide stability when and mixed with epoxy resin and become active fluxing and curing agents only when heated to their melting points.

Other crosslinking agents with fluxing properties which can be used are mono, di-and polyhydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperature. A preferred such compound is adipic dihydrazide. Because of the differing reactivities of polycarboxylic acids and hydrazides, it is preferred to use a mixture of crosslinking agents, such as dodecanedioic acid and adipic dihydrazide, the higher reactivity of the latter being countered by the lower reactivity of the former.

While the oxide removed from the solder or a salt produced by reaction between the polyacid and such oxide, as a result of the fluxing activity of the crosslinking agent, acts as a catalyst for the curing of the polymer, curing in the manner of a snap cure fix is achieved only when a catalyst is present, such catalyst being active at the elevated temperature utilised for soldering. A preferred such latent catalyst is an imidazole catalyst especially phenyl imidazole. This effect is often not desirable as it is contrary to the need to adjust positioning of components during soldering. Other latent reaction catalysts which can be used are tertiary amines with the amine groups optionally substituting the reactive monomer or polymer, as in the aforesaid Araldite MY10510 or MY9512, or metallic salts such as tin octanoate, dibutyl tin dilaurate, ferric acetylacetone, and cobalt (III) acetylacetone.

Preferred compositions will have a thermosetting

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polymer-crosslinking agent/flux content in which there are from 45 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 55 to 30% by weight, more preferably 50 to 40%, by weight crosslinking agent/flux.

5 The use in adhesive compositions employed for encapsulating flip chip connections of ceramic powders to enhance thermal expansion and modulus properties of the composition is preferably to be adopted in the 10 practice of the present invention. It is preferred that such ceramic powders be highly thermally conductive to enhance the connection between solder bump and conductor on the substrate while ensuring that the compositions retain the low viscosity necessary for fluxing and for ease of deposition. The filler is 15 preferably a nominally 5μ diameter spherical ceramic bead or hollow sphere composition. More generally, it may be a glass or ceramic powder comprising spherical particles of $0.1-25\mu$, preferably $1-15\mu$, diameter or comprise essentially monodisperse spherical particles 20 having a single diameter of $0.1-25\mu$, preferably $1-15\mu$. The ceramic powder has preferably a very high thermal conductivity. Examples of such ceramic powders which may be employed are SiO_2 , MgO , Al_2O_3 , TiO_2/ZnO , barium 25 sulphate and diamond dust. In some cases, it is preferred that the ceramic powder utilised has instead a very low or negative coefficient of thermal expansion, too, and if this requirement is imposed on the ceramic powder then a preferred example is 30 aluminium lithium silicate.

Metal oxides formed on solder metals even at ambient temperatures are themselves a problem since they can catalyse crosslinking of the thermosetting resin or its monomer precursor. In accordance with a 35 preferred embodiment of the invention, the resin or precursor contains an acid flux which is liquid at

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temperatures below 100°C, preferably below 40°C, more preferably ambient temperature. This acid will react with oxides to form salts which will not decompose until at elevated temperatures, in particular soldering temperatures when the resulting oxides, together with oxides formed on the metal surfaces more readily at the higher temperatures and removed from the metal surfaces by the flux/crosslinking agent, will catalyse the crosslinking of the thermosetting polymer.

The term "acid" as such is used herein to denote the more volatile flux for preventing prepolymerisation/crosslinking and to distinguish it from the solid crosslinking agent/flux. The more volatile flux is generally liquid at ambient temperature so that it acts immediately as a flux. It should certainly be liquid, at least at temperatures below those at which the crosslinking agents used become fully reactive in the presence of metal oxide/salt crosslinking catalysts. It is thus preferred that the acid used for preventing prepolymerisation, even if solid at ambient temperature, is liquid by 40°C.

Such liquid acids may be polyacids, but will normally be monocarboxylic acids. The acids preferably contain at least 8 carbon atoms and are exemplified by versatic acids, in particular versatic 10 which is a synthetic acid composed of a mixture of highly branched isomers of C₁₀ monocarboxylic acids, mainly of tertiary structure. The high degree of branching gives rise to steric hindrance which means that the salts formed are thoroughly stable and difficult to break down. Other acids which may be used are capric acid, caprylic acid, lauric acid, stearic acid and palmitic acid.

When such monocarboxylic acids are to be used, compositions embodying the invention preferably will have a thermosetting polymer - flux content in which

there are 30 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 70 to 30%, more preferably 50 to 40%, by weight of a mixture of fluxes, the flux components consisting of from 80 to 5 97%, preferably 85 to 95%, by weight of solid crosslinking agent/flux and from 20 to 3%, preferably 15 to 5%, by weight of acid flux which is liquid at below 100°C.

When practising the present invention, there is no 10 need for the adhesive composition to be introduced subsequent to formation of a solder connection with the attendant difficulties identified above. It is possible for the composition to be predeposited, before 15 emplacement and soldering of electronic component to substrate, on either or both of the electronic component and the substrate. As there is no need for a 20 separate fluxing agent to be employed which is not incorporated in the adhesive composition, the presence of the composition on one or other of the electronic component and the substrate fulfils the required 25 fluxing function. Insofar as the composition may be applied to the electronic component, then application may be to dies which are either in wafer form or as separate discrete devices. Application of the composition may be by screen printing, stencil printing, dispensing, spinning or any other known 30 method for applying a composition to discrete areas.

The ease of working in accordance with the method 35 of this invention enables the composition to contain the thermosetting resin in the form of a B-stageable precursor for application to die, substrate or carrier tape and then B-staging so as to form a handleable film which becomes fully crosslinked only when the soldering operation is carried out.

The following examples illustrate the adhesive 35 compositions which may be used in the practice of this

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invention. In the examples all percentages are percentages by weight.

Example 1

ERL 4221 40.6%
5 MY9512 12.7%
DDDA 46.7%

This composition was functionally good and of satisfactory viscosity for most applications.

10 Example 2

ERL 4221 39.65%
Epoxy MY9512 12.40%
DDDA 41.05%
Versatic 10 6.90%

15 This composition was functionally good in not undergoing pre-crosslinking but had too low a viscosity for some applications. As a result, higher viscosity compositions as follows were made up and found to work well.

20 Example 3

ERL 4221 33.45%
MY9512 18.60%
DDDA 41.05%
25 Versatic 10 6.90%

Example 4

ERL 4221 26.05%
MY9512 26.00%
30 DDDA 41.05%
Versatic 10 6.90%

Example 5

ERL 4221 12.40%
35 MY9512 39.65%
DDDA 41.05%

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Versatic 10 6.90%

The initial viscosity of the composition is here somewhat too high for ease of use. Moreover, while Examples 2 to 5 made use of monocarboxylic acids liquid at ambient temperature, it is also possible to use monocarboxylic acids solid at ambient temperature but liquid at temperatures below those at which the crosslinking agent/flux are, for example, as follows:-

10. Example 6

ERL 4221 39.65%

Epoxy MY9512 12.40%

DDDA 41.05%

Prifrac 2960 6.90% (C16 Palmitic acid - solid
melts at 60°C)15. Example 7

ERL 4221 39.65%

Epoxy MY9512 12.40%

DDDA 41.05%

20. Versatic 10 6.90% (C18 - melts at 69°C)

Finally compositions were formulated which contained lower amounts of monocarboxylic acid. These, too, proved to be satisfactory.

25. Example 8

ERL 4221 39.65%

MY9512 12.40%

DDDA 44.95%

30. Versatic 10 3.00%

35. Example 9

ERL 4221 42.62%

MY9512 13.33%

DDDA 41.05%

Versatic 10 3.00%

* CLAIMS OF TEXT
accompanying IPER (pgs 15-21) *

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CLAIMS

1. A thermally curable adhesive composition which comprises:

5 (a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent; and

10 (b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

15 which composition is thermally curable when heated to temperature range extending from the liquidus temperature of the alloy Sn/Pb 60/40 up to the liquidus temperature of the alloy Sn/Pb 3/97 and in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures 20 in the range of from 20-25°C.

2. A composition according to claim 1, wherein the chemical crosslinking agent is solid at ambient 25 temperature.

3. A composition according to claim 2, wherein said chemical crosslinking agent is selected from polyacids, polyanhydrides and hydrazides which are insoluble in the monomer or polymer until heated to soldering 30 temperature.

4. A composition according to claim 3, wherein the polyacid is selected from polymers containing two or 35 more carboxyl groups and di- and polycarboxylic acids and di-and polyanhydrides.

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5. A composition according to claim 4, wherein the polycarboxylic acid is a C₆ or greater dicarboxylic acid.

5 6. A composition according to claim 3, wherein the hydrazide is a monohydrazide, dihydrazide or polyfunctional hydrazide.

10 7. A composition according to any one of claims 3 to 6, wherein the crosslinking agent contains a dihydrazide and/or a dicarboxylic acid.

15 8. A composition according to claim 7, wherein the crosslinking agent contains adipic dihydrazide and/or dodecanedioic acid.

9. A composition according to claim 4, wherein the crosslinking agent is a styrene acrylic acid copolymer.

20 10. A composition according to any preceding claim, which has a thermosetting polymer - solid crosslinking agent/flux content in which there are from 30 to 70% by weight of thermosetting polymer and from 70 to 30% by weight of solid crosslinking agent/flux.

25 11. A composition according to Claim 10, wherein said thermosetting polymer content is from 50 to 60% by weight and said solid crosslinking agent/flux content is from 50 to 40% by weight of the total amount of thermosetting polymer and crosslinking agent/flux.

30 12. A composition according to any one of claims 1 to 11, wherein said polymer is an epoxy resin.

35 13. A composition according to claim 12, wherein said polymer is a B-staged epoxy resin.

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14. A composition according to claim 13, wherein the said polymer is a diglycidyl ether of bisphenol A.

15. A composition according to claim 14, wherein the said polymer is based on a tri- or tetrafunctional epoxide or a difunctional cycloaliphatic epoxide or a mixture of two or more such epoxides.

10 16. A composition according to any preceding claim, which additionally comprises an acid flux which is liquid at temperatures below 100°C.

15 17. A composition according to Claim 16, wherein the acid flux is liquid at temperatures of from 20 to 25°C.

18. A composition according to Claim 16 or 17, wherein the acid flux is a monocarboxylic acid, preferably containing at least 8 carbon atoms.

20 19. A composition according to Claim 18, wherein the acid flux is a versatic acid, capric acid, caprylic acid, lauric acid, stearic acid or palmitic acid.

25 20. A composition according to any one of Claims 16 to 19, which has a thermosetting polymer-flux content in which there are from 30 to 70% by weight of thermosetting polymer and from 70 to 30% by weight of flux, which flux is, in turn, made up from 80 to 97% by weight of said solid crosslinking agent/acid flux and from 20 to 3% by weight of said acid flux.

35 21. A composition according to Claim 20, which has a thermosetting polymer-flux content in which there are from 50 to 60% by weight of thermosetting polymer and from 50 to 40% by weight of flux, which flux is, in turn, made up from 85 to 95% by weight of said solid

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crosslinking agent/flux and from 15 to 5% by weight of said acid flux.

22. A composition according to any preceding claim,
5 which additionally comprises a latent reaction catalyst selected from tertiary amines and imidazoles and metallic salts.

23. A composition according to Claim 22, wherein the
10 imidazole is phenyl imidazole.

24. A composition according to Claim 22, wherein the
tertiary amine is constituted by self catalysing
15 tertiary amine groups substituting the reactive monomer or polymer.

25. A composition according to Claim 24, wherein the
reactive monomer is a tertiary amine-substituted
trifunctional or tetrafunctional epoxide.

20 26. A composition according to Claim 22, wherein the
metallic salt is tin octanoate, dibutyl tin dilaurate,
ferric acetylacetone, and cobalt (III)
acetylacetone.

25 27. A composition according to any preceding claim
which further comprises a thermally conductive filler.

28. A composition according to Claim 27, wherein said
30 filler reduces thermal expansion of the composition.

29. A composition according to Claims 27 and 28,
wherein the filler is constituted by nominally 5 μ
35 spherical ceramic beads or hollow spheres.

30. A composition according to Claim 27, wherein the

filler is a ceramic or glass ceramic powder comprising spherical particles with diameters in the range from 0.1 to 25 μ , preferably 1-15 μ .

5 31. A composition according to Claim 27, wherein the filler is a ceramic or glass ceramic powder consisting essentially of monodisperse spherical particles having a single diameter in the range from, 0.1 to 25 μ , preferably 1-15 μ .

10 32. A composition according to Claim 27, wherein the filler is a thermally conductive ceramic powder.

15 33. A composition according to Claim 32, wherein the ceramic powder is selected from SiO_2 , MgO , Al_2O_3 , TiO_2 / ZnO , barium sulphate and diamond dust.

20 34. A composition according to Claim 27, wherein the ceramic powder has a negative coefficient of thermal expansion.

35. A composition according to Claim 34, wherein the ceramic material is aluminium lithium silicate.

25 36. A method of producing an electronic device which comprises opposing an electrical component having a surface carrying a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition being applied to said surface of the electrical component and/or to the substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the

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substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced in situ from monomer or polymer in the adhesive composition, in which method (1) the thermally curable adhesive composition comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent; and
(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when the material of the solder bump is molten and in the presence of a catalyst for the crosslinking of the polymer with the crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures in the range of 20-25°C and (2) catalysis of crosslinking of the thermally curable adhesive is achieved by metal oxide removed from metal surfaces by the fluxing composition and/or salts formed by reaction between metal oxide and crosslinking agent.

37. A method as claimed in Claim 36, wherein the thermally curable adhesive composition is applied to one and/or both of the said electrical component and said substrate prior to bringing the two together.

38. A method as claimed in Claim 36 or 37, wherein no fluxing agent is applied to either the surface of said electrical component carrying the electrical terminations or to said substrate prior to application of the curable adhesive composition.

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39. A method as claimed in any one of Claims 36 to 38, wherein the thermally curable adhesive composition is applied to dies, which are either in wafer form or as separate discrete devices.

5

40. A method as claimed in any one of Claims 36 to 39, wherein the thermally curable adhesive composition is applied by screen printing, stencil printing, dispensing or spinning.

10

41. A method as claimed in any one of claims 36 to 40, wherein the thermally curable adhesive composition is a composition as claimed in any one claims 1 to 35.

15

42. A method as claimed in any one of Claims 36 to 41, wherein the thermally curable adhesive composition is applied in B-stageable form and B-staged in situ.

**COMBINED DECLARATION
AND POWER OF ATTORNEY**

Attorney Docket No.: 1118-5 PCT/US

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate, § 119(e) of any United States provisional application, or § 365(b) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(d) no such applications have been filed.

(e) such applications have been filed as follows:

**EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day,month,year)	PRIORITY CLAIMED UNDER 35 USC 119
GB	9808587.1	22.04.98	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
GB	9821162.6	29.09.98	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365 (c) of any PCT International application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112.

(f) no such applications have been filed.

(g) such applications have been filed as follows:

APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 120
		<input type="checkbox"/> Yes <input type="checkbox"/> No
		<input type="checkbox"/> Yes <input type="checkbox"/> No

POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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**COMBINED DECLARATION
AND POWER OF ATTORNEY**

Attorney Docket No.: 1118-5 PCT/US

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DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURES

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COMBINED DECLARATION AND POWER OF ATTORNEY
(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION OR CIP)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

original
 design
 supplemental
 national stage of PCT
 continuation
 continuation-in-part (CIP)

INVENTORSHIP IDENTIFICATION

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (*if only one name is listed below*) or an original, first and joint inventor (*if plural names are listed below*) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

Adhesive and Encapsulating Material with Fluxing Properties

SPECIFICATION IDENTIFICATION

the specification of which:

(a) is attached hereto.

(b) was filed on _____ as Application No. _____ or Express Mail Mailing Label No. _____, as Application No. not yet known, and was amended on _____ (*if applicable*).

(c) was described and claimed in PCT International Application No. PCT/GB99/01236 filed on 22.04.99 and as amended under PCT Article 19 on _____ (*if any*).

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations § 1.56(a).

In compliance with this duty, there is attached an information disclosure statement (37 CFR 1.97).